Effect of small rotations of $\mathbf{G}$ away from $\mathbf{b}$. The transformations of the magnetic field ($\mathbf{H}$), the order parameter ($\mathbf{G}$) and the electric field ($\mathbf{E}$) under the generators of $\text{Pnma}$ (modulo primitive translations) are shown in Tab. SI and in Tab. I in the text. The invariant terms in the free energy, $\Phi$, leading to linear magnetoelectric couplings can be written as

$$
\Phi_{ME} = G^a (\lambda^a || H^a E^a + \lambda^a || H^b E^b + \lambda^a || H^c E^c) + G^b (\lambda^b || H^b E^a + \lambda^b || H^a E^c) + G^c (\lambda^c || H^c E^a + \lambda^c || H^a E^c),
$$

where $\lambda^a$, $\lambda^b$, and $\lambda^c$ are functions of temperature. From Eq. (S1) it is clear that different components of the magnetoelectric tensor correspond to different components of $\mathbf{G}$ along the crystallographic axes. Therefore, a small rotation of $\mathbf{G}$ from the $\mathbf{b}$ direction does not affect the analysis of $\alpha_0$ and $\alpha_\perp$ performed in the text with the assumption of $\mathbf{G} \parallel \mathbf{b}$.

Symmetry analysis of $\Lambda^{ab}_i$ and $\partial E_{\alpha} \Lambda^{ab}_i$ extended to three electric field orientations. The effect of the generators of $\text{Pnma}$ on $\Lambda^{ab}_{\alpha\beta}$ can be obtained considering the transformations of the magnetic sublattices (see Tab. I in the text) and the transformations of $\mathbf{L}$. Table SII shows the way in which $\Lambda^{ab}_{\alpha\beta}$ changes under these generators (modulo primitive translations). These transformations imply constraints on some of the $\Lambda^{ab}_{\alpha\beta}$ components at each magnetic sublattice. For instance, the invariance under inversion, $I$, gives: $\lambda_{1}^{ab} = \lambda_{3}^{ab}$ and the invariance under two-fold rotation around $\mathbf{b}$ implies: $\lambda_{1}^{ab} = -\lambda_{4}^{ab}$ which can be both satisfied only for $\Lambda_{1}^{ab} = \Lambda_{4}^{ab} = 0$. Similarly, using Tab. SII, one finds: $\Lambda_{2}^{ab} = \Lambda_{2}^{ab} = 0$, $\Lambda_{2}^{ab} = \Lambda_{2}^{ab} = \Lambda_{4}^{ab} = 0$, and $\Lambda_{4}^{ab} = \Lambda_{4}^{ab} = 0$. A small applied electric field affects the orbital moments by changing $\Lambda^{ab}_{\alpha\beta}$. The expansion of orbital magnetic moment at the $i$-th sublattice, $\mu_{(L)i}$, to the linear order in $\mathbf{E}$ gives

$$
\mu_{(L)i} = -\lambda \mu_B \left( \Lambda_1^{ab} (0) + \sum_{\mu = a,b,c} \frac{\partial \Lambda^{ab}_i}{\partial E^\mu} E^{\mu} + \ldots \right) \langle S^b \rangle,
$$

where the second term inside the brackets contains the derivatives given in Eq. (3) in the text.

The relative changes of orbital magnetic moments on different sublattice due to an applied electric field are determined by the symmetry properties of $\frac{\partial \Lambda^{ab}}{\partial E^\mu}$. These are listed in Tab. SII and are obtained by combining transformations of $\mathbf{E}$ with those of $\Lambda^{ab}_{\alpha\beta}$ under the generators of $\text{Pnma}$. Similarly to the case of $\Lambda^{ab}_i$, symmetries impose constraints on $\frac{\partial \Lambda^{ab}}{\partial E^\mu}$. For example, the set of equations: $\partial E_{\alpha} \Lambda_{1}^{ab} = -\partial E_{\alpha} \Lambda_{4}^{ab}$ and $\partial E_{\alpha} \Lambda_{2}^{ab} = \partial E_{\alpha} \Lambda_{3}^{ab}$, which need to be satisfied to ensure, respectively, the invariance under inversion and two fold rotation along $\mathbf{b}$ (see Tab. SII), imply that $\partial E_{\alpha} \Lambda_{1}^{ab} = \partial E_{\alpha} \Lambda_{4}^{ab} = 0$. Analogously, we obtain that $\partial E_{\alpha} \Lambda_{1}^{ab} = \partial E_{\alpha} \Lambda_{3}^{ab} = \partial E_{\alpha} \Lambda_{2}^{ab}$ and $\partial E_{\alpha} \Lambda_{4}^{ab}$ have to vanish at each magnetic sublattice. Furthermore, the non-vanishing terms must satisfy:

$$
\begin{align*}
\partial E_{\alpha} \Lambda_{1}^{ab} &= -\partial E_{\alpha} \Lambda_{2}^{ab} = -\partial E_{\alpha} \Lambda_{3}^{ab} = -\partial E_{\alpha} \Lambda_{4}^{ab} \\
\partial E_{\alpha} \Lambda_{2}^{ab} &= \partial E_{\alpha} \Lambda_{3}^{ab} = \partial E_{\alpha} \Lambda_{4}^{ab} \\
\partial E_{\alpha} \Lambda_{3}^{ab} &= -\partial E_{\alpha} \Lambda_{2}^{ab} = \partial E_{\alpha} \Lambda_{4}^{ab} \\
\partial E_{\alpha} \Lambda_{4}^{ab} &= -\partial E_{\alpha} \Lambda_{1}^{ab} = -\partial E_{\alpha} \Lambda_{3}^{ab} = -\partial E_{\alpha} \Lambda_{2}^{ab}.
\end{align*}
$$

The first two sets of equations in Eq. (S3) together with Eq. (S2) and the sign of the components of the spins along $b$ at every magnetic sublattice shows that an applied electric field along $\mathbf{a}$ ($\mathbf{b}$) induces a net orbital moment along $\mathbf{b}$ ($\mathbf{a}$).

In the same way, from the last equation in Eq. (S3) one can derive that an applied electric field along $c$ affects the orbital magnetic moments along $\mathbf{b}$ of sublattice 1 and 4 in the opposite way to those of sublattices 2 and 3 giving rise to a zero net magnetization. However, the staggered orbital magnetization $C_L = \mu_{(L)1} - \mu_{(L)2} - \mu_{(L)3} + \mu_{(L)4}$ along $\mathbf{b}$ should by symmetry depend linearly on the applied electric field. To check this we perform the same calculations described in the text but for $\mathbf{E} \parallel \mathbf{c}$. The obtained electric field dependence of $C^b$ for $J = 1$ eV is plotted in Fig. S1(a) and shows that such response is approximately double that of the orbital magnetization described in the text. In the same way we expect a linear

TABLE SI: Transformation of the magnetic field $\mathbf{E}$ and the order parameter under the generators of the point group of $\text{Pnma}$. | $J$ | $I$ | $2_a$ | $2_b$ |
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TABLE II: Transformation of tensor $\Lambda_i^{ab}$ and its derivatives with respect to the electric field under the generators of $P\text{nma}$ (modulo a primitive translation). The superscript indices label the coordinate while the subscript index labels the magnetic sublattice.

<table>
<thead>
<tr>
<th>$\Lambda_i^{ab}$</th>
<th>$\partial E \Lambda_i^{ab}$</th>
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FIG. S1: Electric field dependence of $C(E)$ (a) for $J = 1$ eV (blue dots). (b) $J$ dependence of the size of orbital moments at each magnetic sublattice for $U = 4$ eV (blue dots) and $U = 5$ eV (red dots). (c) Size of the orbital moment as a function of integration sphere volume for $E = 0$ V/Å (blue dots) and $E = 0.06$ V/Å (green triangles and red squares). The lines are guides for the eyes.

dependence of $C(E)$ on $E \parallel b$. However, such dependence is so weak that, as mentioned in the text, the changes in orbital moments are above numerical resolution only at $E = 0.06$ V/Å.

We also note that the size of orbital moments strongly depends on the values of the on-site Coulomb interaction $U$ and on the effective on-site exchange parameter $J$. Figure S1(b) shows the size of calculated orbital magnetic moment at $E = 0$ as a function of $J$ for $U = 4$ eV (blue dots) and $U = 5$ eV (red dots).

Convergence of the orbital moment. Finally, we analyze the convergence of the local orbital moments with respect to the radius of the spheres in which they are evaluated. The modulation of this radius in VASP would require the generation of new pseudo-potentials, which is not an easy task. Hence we decided to use an all-electron method based on linear augmented plane waves (LAPW), namely ELK [1], which allows to alter the radius of the projection spheres. First, we compared orbital moments using both methods and the same radius of the spheres finding that in the ground-state structure their values agree up to $10^{-4} \mu_B$. Next, we varied the radius of the spheres in the ELK code. For this test, we used a GGA exchange correlation potential to avoid any additional influence of the Hubbard $U$ applied within the sphere. Figure S1(c) shows the obtained value of orbital moments as a function of sphere volume at two Fe sub-
lattice sites for the case of $E = 0$ (blue squares) and $E^b = 0.06 V/A$ (red squares and green triangles). While the orbital moment increases approximately linearly with sphere radius over the investigated range, the difference of the orbital moment is constant, so we can conclude that the response is well converged even at the smallest sphere radii. It is worth mentioning that the orbital moment response obtained using GGA is smaller than that from with LDA+$U$. This finding may be attributed to a volume effect since the structure used was not optimized for GGA.

Additional technical details. All VASP density functional calculations were performed with an energy cut-off $E_{cut} = 600$ eV. The ionic relaxation, the calculation of the force constant matrix and the calculations of the orbital magnetism were done using a $2 \times 4 \times 4$ Monkhorst-Pack k-point mesh. The Born effective charges were obtained using both the finite electric field method (after relaxation using $4 \times 4 \times 4$ gamma centered k-point mesh) and density functional perturbation theory (with a $2 \times 4 \times 4$ Monkhorst-Pack k-point mesh). The results obtained with the two procedures had minimal differences. The force constant matrix was obtained using finite displacements method obtained through the software Phonopy [2]. In the LAPW ELK calculation we used a $3 \times 5 \times 5$ k-point mesh and iterated the density until the change in potential was smaller than $10^{-6}$ eV.